

PATENT SPECIFICATION

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(54) HALONIUM SALTS

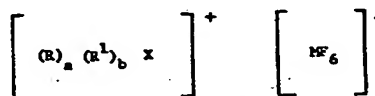
(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12345, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improvements in salts which can be used with epoxy resin compositions for curing by exposure to radiant energy.

Epoxy resins have generally been employed in a variety of applications requiring high performance materials. Cure of an epoxy resin can generally be achieved by two package systems based on the incorporation into the resin of active amine containing compounds or carboxylic acid anhydrides. These systems require thorough mixing of the ingredients; in addition, cure time can be several hours.

Another catalyst which can be used to cure epoxy resins as "one package" systems is based on the employment of a Lewis Acid catalyst in the form of an amine complex such as boron trifluoride-monoethylamine. The Lewis Acid is released on heating; cure takes place within 1 to 8 hours and can require a temperature of 160°C. and higher. As a result, these one package epoxy compositions cannot be employed to coat heat sensitive devices such as delicate electronic components. Nor can epoxy monomers having low boiling points be used due to the resulting losses to evaporation during cure.

As shown by Schlesinger U.S. Patent 3,703,296, certain photosensitive aromatic diazonium salts can be employed to cure epoxy resins. When photolyzed, these aromatic diazonium salts are capable of releasing, *in situ*, a Lewis Acid catalyst which can initiate the rapid polymerization of the epoxy resin. However, even though these one package epoxy resin mixtures can provide fast curing compositions, a stabilizer must be used to minimise cure in the dark during storage of these mixtures. Despite these measures, gellation of the mixture can occur even in the absence of light. In addition, nitrogen is released during UV-cure, which can result in film imperfections. Diazonium salts are generally thermally unstable, rendering the use of such materials hazardous because of the possibility of runaway decomposition. Accordingly the present invention provides a salt for use in curing curable compositions, the salt having the formula:

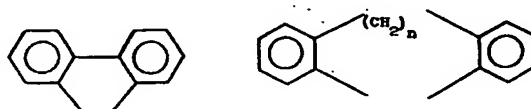


where M is P, As or Sb, R is a monovalent aromatic organic radical, R¹ is a divalent aromatic organic radical, X is a halogen radical, a is 0 and b is 1 or a is 2 and b is 0.

Radicals included by R can be the same or different, aromatic carboxylic or heterocyclic radical having from 6 to 20 carbon atoms, which can be substituted with from 1 to 4 monovalent radicals selected from for example, C₁₋₄ alkoxy, C₁₋₄ alkyl, nitro and chloro; R is more particularly, phenyl, chlorophenyl, nitro-

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phenyl, methoxyphenyl, or pyridyl. Radicals included by R^1 are divalent radicals such as



where n is an integer. Halonium salts included in the formula are, for example:



The halonium salts of this invention can be made by the procedures, suitably modified, described by O. A. Ptitsyna, M. E. Pudcva, et al, Dokl. Akad. Nauk, SSSR, 163 383 (1965); Dokl., Chem., 163 671 (1965). F. Marshall Beringer, M. Drexler, E. M. Gindler, et al, J. Am. Chem. Soc., 75 2705 (1953).

Thus to prepare the hexafluoro salts of this invention, metathesis of a corresponding iodonium salt is conducted, for example, by reacting 0.32 g. of diphenyl iodonium chloride with 0.21 g. of sodium hexafluoroarsenate at 50°C for 20 minutes in 10 g. of limonene dioxide. The salts are allowed to settle and the clear supernatant liquid is drawn off. Other salts can be made in an analogous manner.

The term "epoxy resin" as utilized herein includes any monomeric, dimeric or oligomeric or polymeric epoxy material containing one or a plurality of epoxy functional groups. For example, those resins which result from the reaction of bisphenol-A (4,4'-isopropylidenediphenol) and epichlorohydrin, or by the reaction of low molecular weight phenol-formaldehyde resins (Novolak resins) with epichlorohydrin, can be used alone or in combination with an epoxy containing compound as a reactive diluent.

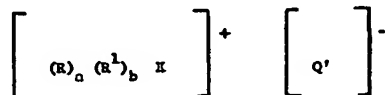
Such diluents as phenyl glycidyl ether, 4-vinylcyclohexene dioxide, limonene dioxide, 1,2-cyclohexene oxide, glycidyl acrylate, glycidyl methacrylate, styrene oxide and allyl glycidyl ether may be added as viscosity modifying agents.

In addition, the compounds cured by the salts can be extended to include polymeric materials containing terminal or pendant epoxy groups. Examples of these compounds are vinyl copolymers containing glycidyl acrylate or methacrylate as one of the comonomers. Other classes of epoxy containing polymers amenable to cure using the above catalysts are epoxy-siloxane resins, epoxy-polyurethanes and epoxypolyesters. Such polymers usually have epoxy functional groups at the ends of their chains. Epoxy-siloxane resins and method for making are more particularly shown by E. P. Plueddemann and G. Fanget, J. Am. Chem. Soc. 81 632-5 (1959). As described in the literature, epoxy resins can also be modified in a number of standard ways such as reactions with amines, carboxylic acids, thiols, phenols, alcohols, etc. as shown in U.S. patents 2,935,488; 3,235,620; 3,369,055; 3,379,653; 3,398,211; 3,403,199; 3,563,850; 3,567,797; and 3,677,995. Further examples of epoxy resins which can be used are shown in the Encyclopedia of Polymer Science and Technology, Vol. 6, 1967, Interscience Publishers, New York, pp 209-271.

The curable compositions are further described in our Patent Specification No. 15704/75 (Serial No. 1,516,351) and can be made by blending the epoxy resin, which hereinafter will signify epoxy monomer, epoxy prepolymer, oxirane containing organic polymers or a mixture thereof, with an effective amount of the halonium salt. The resulting curable composition which can be in the form of a varnish having a viscosity of from 1 centipoise to 100,000 centipoises at 25°C can be applied to a variety of substrates by conventional means and cured to the tack-free state within 1 second or less to 10 minutes or more. In other instances, where the epoxy resin is a solid, the curable composition can be a free flowing powder.

Depending upon the compatibility of the halonium salt with the epoxy resin,

the halonium salt can be dissolved or dispersed therein along with an organic solvent such as nitro-methane and acetonitrile prior to its incorporation. In instances where the epoxy resin is a solid, incorporation can be achieved by dry milling or by melt mixing. *In situ*, preparation of the halonium salt by separate or simultaneous incorporation of halonium salt of the formula:



where R, R¹, X, a and b are as previously defined, and Q' is an anion such as Cl⁻, Br⁻, F⁻, I⁻, HSO₄⁻, CH₃SO₃⁻ or NO₃⁻ with the salt of a Lewis Acid of the formula:



also has been found to be effective, where M is as defined above and M' is a metal cation such as Na⁺, K⁺, Li⁺, Ca⁺⁺, Mg⁺⁺, Fe⁺⁺, Ni⁺⁺ and Co⁺⁺, Zn⁺⁺. M' also can be an organic cation such as ammonium group and pyridinium group. Examples of M'(MF₆) are KAsF₆, NaSbF₆ and KPF₆.

Experience has shown that the proportion of halonium salt to the epoxy resin can vary widely inasmuch as the salt is substantially inert, unless activated. Effective results can be achieved, for example, if a proportion of from 0.1% to 15% by weight of halonium salt is employed, based on the weight of curable composition. Higher or lower amounts can be used, however, depending upon factors such as the nature of epoxy resin, intensity of radiation, and cure time desired.

The curable compositions may contain inactive ingredients such as inorganic fillers, dyes, pigments, extenders, viscosity control agents, process aids and UV-screens, in amount of up to 100 parts filler per 100 of epoxy resin. The curable compositions can be applied to such substrates as metal, rubber, plastic, molded parts or films, paper, wood, glass, cloth, concrete and ceramic.

Some of the applications in which the curable compositions of the present invention can be used are, for example, protective, decorative and insulating coatings, potting compounds, printing inks, sealants, adhesives, photoresists, wire insulation, textile coatings, laminates, impregnated tapes and printing plates.

Cure of the curable composition can be achieved by activating the halonium salt to provide the release of the Lewis Acid catalyst. Activation of the halonium salt can be achieved by heating the composition at a temperature in the range of from 150°C to 250°C. Preferably cure can be achieved by exposing the curable composition to radiant energy such as electron beam or ultraviolet light.

In order that those skilled in the art will be better able to practice the invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

EXAMPLE 1.

There was added a cooled solution of about 100 ml of acetic anhydride and 70 ml of concentrated sulfuric acid to a suspension of 100 g of potassium iodate in 100 ml of acetic anhydride and 90 ml of benzene. During the addition, the mixture was stirred and maintained below 5°C. When the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 48 hours. There was then added 400 ml of distilled water. The aqueous portion of the reaction mixture was extracted three times with diethyl ether and petroleum ether to remove unreacted organic materials. A pale yellow crystalline product formed upon addition of ammonium chloride to the aqueous reaction mixture. There was obtained a 48% yield of diphenyliodonium chloride having a m.p. of 180—185°C. The pure salt had a m.p. of 228—229°C.

A mixture of 20 g of moist, freshly prepared Ag₂O, 10 m. of water and 31.6 g of diphenyliodonium chloride was ground together in a slurry. The wet mixture was filtered and washed with water to produce 360 ml of filtrate. The filtrate was cooled until a substantial amount of the solution had frozen. There was slowly added 25 ml (60%) hexafluorophosphoric acid cooled to -15°C. The cold solution was stirred and allowed to warm to room temperature. A white crystalline solid separated and was collected by filtration. There was obtained a 74% yield of diphenyliodonium hexafluorophosphate m.p. 139—141°C when the solid was dried overnight *in vacuo* at 60°C.

A curable composition was prepared by dissolving 0.05 part of diphenyliodonium hexafluorophosphate in a small amount of acetonitrile and mixing the resulting solution in 5 parts of 4-vinylcyclohexene dioxide.

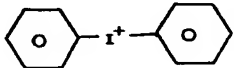
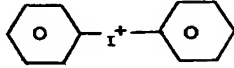
The viscosity of the resulting curable composition did not change substantially after several months exposure under normal room lighting.

A portion of the curable compositions was applied as 0.1 mil onto a steel strip. The treated steel surface was exposed 15 seconds to the ultraviolet radiation of an H3T7 lamp at a distance of 2 inches. A clear tack-free film was formed which showed no signs of bubbles or other imperfections.

The above treated strip was then immersed in 10C hydrocarbon oil for 48 hours at 120°C to determine its hydrolytic stability in accordance with IFT test ASTM D971-50 Interfacial Tension of Oil Against Water shown on page 322 of the 1970 Annual Book of ASTM Standards, part 17 (November). In order to pass a reading of at least 30 is required. Satisfactory values were obtained.

EXAMPLES 2 and 3.

Two curable compositions were prepared in accordance with the procedure shown in Example 1 using 4-vinylcyclohexene dioxide and about 3% by weight of the halonium salt. Various cure times were experienced when the compositions were applied onto a glass substrate and cured at a distance of four inches from a GE H3T7 lamp. The following shows the halonium salt used, its m.p. and the cure times.

Examples	Cation	Anion	Mp. (°C)	Cure Time* (min)
2		PF ₆ ⁻	138-141	0.5
3		SbF ₆ ⁻	57-58 imp.	0.5

* Time required to cure a 2 mil film containing 3% of the salt at a distance of 4 inches from a G. E. H3T7 lamp.

EXAMPLE 4.

To 10 g limonene dioxide were added 0.32 g diphenyliodonium chloride and 0.21 g sodium hexafluoroarsenate. This mixture was heated for 20 minutes at 50°C to achieve metathesis. The salts were allowed to settle and the clear supernatant liquid was drawn off. The sensitized epoxy compound was applied to a steel strip to a thickness of 2 mil and exposed to UV light as described above. Cure took place in 30 seconds. A tough film having good adhesion to the steel plate was obtained.

EXAMPLE 5.

Three parts of diphenyliodonium hexafluoroarsenate were dissolved in 6.7 parts of methylene chloride and the solution added to 97 parts glycidyl acrylate. A 3 part aliquot of this highly fluid mixture was placed in an aluminum cup and then exposed to the ultraviolet irradiation of a H3T7 lamp using a water filter. The cure time was 15 seconds. Subsequent analysis showed that the conversion to polymer was greater than 95%. A hard glossy resin was obtained.

EXAMPLE 6.

A mixture of 50 parts bisphenol-A-diglycidyl ether and 50 parts (3,4-epoxycyclohexyl)methyl-3,4-epoxycyclohexanecarboxylate was stirred until homogeneous and then 3 parts by weight diphenyliodonium hexafluoroantimonate in a small amount of methylene chloride was added and the solution thoroughly mixed.

A portion of the above sensitized solution was coated onto a steel plate using a 0.2 mil drawbar. The plate was then irradiated for 10 seconds using a GE H3T7 mercury arc lamp at a distance of six inches. The completely cured, hard, glossy film had excellent adhesion to the steel and could not be removed by rubbing it with acetone.

EXAMPLE 7.

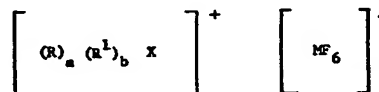
A blend of epoxy resins consisting of 50 parts 4-vinylcyclohexane dioxide, 40 parts of a novolak-epoxy resin having an epoxy equivalent weight of 172—178 and 10 parts n-decylglycidyl ether were thoroughly mixed together. A 100 part aliquot was taken and 1 part diphenyliodonium hexafluoro phosphate was added and the resulting mixture stirred until the catalyst had dissolved. When the above mixture was coated onto a 3 in x 6 in panel and then exposed to a 450 watt medium pressure mercury arc lamp at a distance of 3 inches, a glossy, dry coating was obtained in 3 seconds. The coating withstood attack by hot boiling water for four hours and could not be removed by rubbing with acetone.

EXAMPLE 8.

A mixture was prepared consisting of by weight 67% of a novolak-epoxy resin having an epoxy equivalent weight of 172—178, 33% 4-vinylcyclohexene dioxide, 0.5% of a surface active agent, and 1% diphenyliodonium hexafluoroarsenate. The mixture was applied as a 0.1 mil film to 3 in x 6 in steel plates. The treated plates were exposed for 20 seconds at a distance of 4 inches from a GE H3T7 medium pressure mercury arc lamp. Panels were subsequently immersed for 5 hours at room temperature in methylene chloride; others were immersed for 4 hours in acetone. In all cases, no visible signs of attack on the coating by these agents were observed. The panels were baked for 1 hour at 160°C, then tests were run separately in boiling 5% KOH solution for 30 minutes and in boiling distilled water for 4 hours. At the end of these tests, the coatings were intact and showed no signs of degradation.

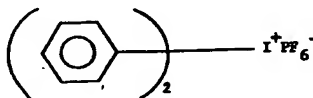
WHAT WE CLAIM IS:—

1. A salt having the formula

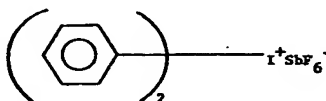


where M is P, As or Sb, R is a monovalent aromatic organic radical, R¹ is a divalent aromatic organic radical, X is a halogen radical, a is 0 and b is 1 or a is 2 and b is 0.

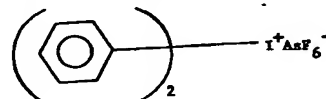
2. A salt as claimed in claim 1 where M is P and X is I.
3. A salt as claimed in claim 1 having the formula:



4. A salt as claimed in claim 1 having the formula:



5. A salt as claimed in claim 1 having the formula:



6. A salt as claimed in claim 1 substantially as hereinbefore described in any one of the examples.

PAUL M. TURNER,
Agent for the Applicants.

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